

## REMARKS

### Support for amendments

New claims 35 and 36 are based on original claims 7 and 17, respectively.

New claims 35 and 36 specify that in step (b) that a reducing agent "consisting of a silylating agent" is introduced. This is supported throughout the specification, in particularly in the experimental section on pages 21-25 and in Figures 4-7. These sections of the application describe a process in which the only reducing agent is a silylating agent.

New claims 35 and 36 additionally specify that steps (b) and (c) are performed after the preceding steps ((a) and (b), respectively), thereby requiring steps (a), (b) and (c) to be performed sequentially. The sequential nature of these reactions appears throughout the specification, including at page 11 lines 8-11; page 12 lines 15-18; and page 13 lines 12-14. Figures 4-6 and accompanying text (page 13-15) illustrate changes in surface species as the reactions are sequentially performed.

New claims 35 and 36 also specify that a surface containing silane moieties is surface species is formed after step (c). Support for this is found at page 6 lines 2-8 and especially in Figures 4-7 (showing experimental verification of those surface species).

New claims 35 and 36 now specify that reaction steps (b) and (c) are repeated one or more times. The idea that the film-producing reactions are to be repeated is expressed throughout the specification, notably at page 6 lines 9 *et. seq.*

New claims 35 and 36 also specify that in each (b)/(c) reaction cycle, a metal film layer is deposited that corresponds in thickness substantially to the atomic spacing of the metal. This is described at page 6 lines 9-20 of the specification.

### The Invention

The invention as now claimed is to a method of producing thin metal films on a substrate. The film is produced by reducing certain metal halides using a gaseous silylating agent. This reaction produces a metal, which is deposited as a thin film at the surface of the substrate. The by-product is a silyl halide, which is a gas that is removed from the reaction zone.

The amended claims specify how this reaction is conducted. The overall metal halide/silylating agent reaction is broken down into two half reactions. These half-reactions

are conducted separately and sequentially, by alternately introducing one of the reactants, then the other. In each case, the reactant is introduced as a gas.

In the amended claims, steps (b) and (c) now clearly require that the respective reagents react with surface species formed in the preceding step. In step (b), the silylating agent reacts with surface metal halide species from the immediately preceding step (a) or (c). In step (c), the metal halide reacts with silane species formed in the immediately preceding step (b).

Processes of the type now claimed are now sometimes referred to as "atomic layer deposition" or "ALD" processes. This is because each reactant forms approximately a monoatomic layer on the substrate surface. Each cycle of reactions therefore forms a metal film corresponding in thickness to substantially the atomic spacing of the metal, as is specified in claims 35 and 36. This process therefore allows for (1) the formation of extremely thin films; (2) exceptionally fine control over the metal film thickness (by repeating the reaction sequences the desired number of times); and (3) the formation of a metal film having a surface that conforms very closely to the surface characteristics of the underlying substrate.

This invention solves several problems. One problem is the need to form ultrathin, high quality metal films on various substrates. Another problem is to make those films at a controlled thickness. A third problem is to make high purity metal films, and in particular films that have minimal silicon and halide contamination. A fourth problem is to make the film under reasonable production conditions, so that substrate thermal damage is minimized and a larger range of substrates can be used.

#### Chemical Vapor Deposition

Chemical vapor deposition (CVD) is another process for forming thin metal films. This process is superficially similar to ALD processes, in that the films are prepared by introducing gaseous reactants into a reaction chamber, where they deposit on the substrate surface and form a film. Early ALD processes were sometimes referred to as variants of CVD processes. The Kobayashi, Bean and Tsai references cited by the examiner all describe CVD processes.

CVD processes differ from ALD, in that in CVD, the reactants are introduced together rather than separately, as in ALD. In CVD, the reactants form droplets in the vapor phase. These droplets then deposit onto the substrate surface, where the metal-

forming reactions are completed. Because of the droplet formation, CVD-deposited metal layers tend to be much thicker than ALD-deposited layers and have comparatively rougher surfaces. The roughness problem with CVD is identified in the Tsai and Bean references, at least. Control over thickness is less accurate, as coating thickness depends on the size and uniformity of the droplets that form.

Regarding the Rejection under 35 USC §102(e) over Kobayashi

Kobayashi describes a CVD process for depositing various metal films. The reactants in the CVD process are a metal halide gas and a fluoro-silane.

As acknowledged by the examiner, Kobayashi does not describe an ALD process as currently claimed, nor does Kobayashi describe any process in which metal layers corresponding in thickness to approximately the atomic spacing of the layer can be produced.

In making the rejection, the examiner pointed out that claims 7 and 17 did not explicitly require that the various reaction steps be conducted separately. Claims 35 and 36 now expressly require steps (a), (b) and (c) to be conducted one after the other, and therefore distinguish this reference.

Regarding the Rejections of under 35 USC §103 over Izumi in view of Bean (and other secondary references)

These rejections are respectfully traversed.

Although applicants will respond to the substance of this rejection, the Bean reference has not been established as prior art to this application. This article was apparently downloaded from an Internet website on August 4, 2003, which is well after the effective filing date of this application. Although the text of the document bears a November 6, 1998 date, this date does not appear to be a publication date or any other indication that this document was in the public domain, and therefore available as prior art, on November 6, 1998 or any other date before the effective filing date of this application. The reference contains no indicia on its face that it was published anywhere other than by being posted to the [www.frii.com/~bean](http://www.frii.com/~bean) web page.

It also cannot be ascertained from the document itself, or the [www.frii.com/~bean](http://www.frii.com/~bean) web page, when the document was posted to the web page. The web page itself indicated that it was last updated on October 4, 2000. Even if this date is accurate (which cannot be

assumed), it is after the effective filing date of this application, and suggests that this document may have been posted to the web page at any time up to and including October 4, 2000.

There are few if any controls over the content of individual websites. The procedures that ensure the reliability of dates of more traditional publications are lacking on these sites. As a result, dates at which documents are published on web pages can be unreliable and unverifiable, especially when content is accessed (as in this case) long after the critical dates.

As to the substance of the rejection, the Izumi reference was discussed at length in the previous response. Izumi uses a sequence of reactions to form a tungsten coating, but explicitly teaches away from using a silylating agent to reduce tungsten halide to form the metal. Instead, Izumi uses hydrogen as the reducing agent. This is because the use of silane reducing agents had been reported to produce poor quality films in CVD processes. See column 1 of Izumi.

One desiring to form high quality tungsten films would, on the basis of Izumi, be discouraged from using the approach now claimed (as Izumi himself was), because of the CVD experience that Izumi describes, in which tungsten made using silane reducing agents was contaminated with silicon.

At page 9 of the office action, the Examiner acknowledged that Izumi by itself was insufficient to sustain the rejection of the claims. The examiner therefore now relies on the Bean reference to overcome the deficiencies of Izumi.

Bean describes using hydrogen/tungsten halide and silane/tungsten halide CVD processes to deposit tungsten films on silicon substrates. In the abstract, Bean describes producing tungsten films on silicon by first producing a CVD "seed" layer by silane reduction of tungsten hexafluoride, and then depositing a CVD "bulk" layer by hydrogen reduction of tungsten hexafluoride.

The reasons Bean suggests this approach are two-fold. First, silane reduction of tungsten hexafluoride in a CVD process exhibits poor step coverage, loss of selectivity and silicon contaminated films. (See the first page, last four lines.) Note that this last problem is the same problem identified by Izumi when silanes are used to reduce tungsten halides in CVD processes. Second, hydrogen tends to attack silicon substrates. Thus, according to Bean, neither the hydrogen-based nor the silane-based CVD processes are suitable alone. She suggests skirting the problem by first depositing a "seed" layer via  $WF_6$ /silane CVD.

Although the resulting film has the noted deficiencies, it is adequate to serve as a barrier layer that protects the silicon substrate from attack by hydrogen when the second,  $WF_6$ /hydrogen CVD layer is applied. The  $WF_6$ /hydrogen CVD layer is of high enough quality to perform its needed function.

Note that neither of Bean's steps involve an ALD process. Bean process involves forming a first tungsten CVD "seed" layer using  $WF_6$  and silane, and then a second, separate CVD layer using  $WF_6$  and hydrogen. Bean does not describe carrying out sequential half-reactions as set forth in claims 35 and 36.

Both references agree that in CVD processes, silane reducing agents produce films that are contaminated with silicon and which are therefore inferior. Neither of these references forms any basis upon which to suggest that by changing the deposition process to an ALD process, the quality problem reported by Izumi and Bean could be overcome, and good quality tungsten films could be made even when using a silane reducing agent.

The applicants have found that in an ALD process, silane reducing agents can be used to produce very high quality metal films. Notably, the films are essentially free of silicon contamination. This is described in the specification at page 20, lines 8-13. As noted in the previous response, later papers published by Drs. Klaus and/or George provide additional experimental verification of this phenomenon.

There is nothing in the Izumi or Bean references, whether taken individually or together, which would suggest that good quality metal films could be made in any process using silanes as a reducing agent. Izumi simply assumes that tungsten/silane ALD will not work, based on prior experience with tungsten/silane CVD, and teaches directly away from using silanes as a reducing agent in an ALD process. Bean also takes for granted that films deposited in a tungsten/silane CVD process will be of poor quality. Her suggestion for overcoming this is to restrict the use of tungsten/silane CVD to forming a "seed" layer, which is then covered with a tungsten/hydrogen CVD layer. Taken together, the clear message to one of ordinary skill in the art is that tungsten/silane processes will not result in good quality films.

In the interview conducted January 13, 2004, the examiner expressed a concern that the claims would read on that portion of Bean's teaching in which a tungsten/hydrogen CVD layer was applied atop a tungsten/silane CVD "seed" layer. The concern seems to be that Bean's "seed" layer might produce a tungsten film that has surface silane species which would react with tungsten halide that is introduced in the subsequent

tungsten/hydrogen CVD layer. However, Bean does not describe this as happening. Even if that were true to some extent, Bean does not describe any process in which the sequential half-reactions are repeated sequentially as required by the instant claim. Bean's CVD processes deposit a thick tungsten layer formed by tungsten/hydrogen CVD layer atop another thick (compared to ALD monlayer films) tungsten "seed" layer formed by a tungsten/silane CVD. Bean's process does not form layers having a thickness corresponding substantially to the atomic spacing of the metal.

As discussed in the earlier response, the additional secondary references do not overcome the basic deficiencies of the Izumi and Bean references.

Regarding the rejections over Leem in view of Tsai (and other secondary references)

These rejections are respectfully traversed. As discussed in the previous response, Leem's process is limited to forming aluminum films. This point has been acknowledged by the examiner at page 8 of the last office action.

As also pointed out in the last response, there is strong basis to doubt Leem's teachings. Lee et al., "Atomic Layer Deposition of Aluminum Thin Films Using an Alternating Supply of Trimethylaluminum and a Hydrogen Plasma", *Electrochemical and Solid-State Letters*, 5 (10) C91-93 (2002), show that attempted deposition of aluminum from trimethylaluminum and hydrogen does not occur under the conditions employed (*see* paragraph bridging the columns of page C91). Lee et al. established that a hydrogen plasma is needed to be created in order for the deposition of aluminum to occur. Leem itself contains no experimental section, nor does he report any results that would contradict Lee's work.

Tsai describes a CVD process for making tungsten films, not aluminum films. Thus, in order to combine Tsai and Leem to arrive at applicant's invention, one must first ignore the fact that Leem's teachings are limited to aluminum. Then one must ignore the subsequent work of Lee, showing that Leem's process will not work unless special conditions, not disclosed in Leem, are employed, keeping in mind that Leem himself offered no experimental verification of his claims. Then one must ignore the fact that the Tsai's tungsten-CVD process itself bears little resemblance to Leem's process, and that Tsai provides no reason to suggest that his process is applicable to depositing aluminum films. The combination of these references does not establish a *prima facie* case of unpatentability of the applicant's claims.

Regarding the rejection based on Tsai in view of Srinivasan and Kobayashi.

This rejection is respectfully traversed. Tsai describes a CVD process for depositing tungsten films. In his process, a tungsten layer is applied to a substrate (in a CVD process that is not described but which apparently uses  $WF_6$  as a reactant). A thinner polysilicone layer is then applied overtop of the tungsten layer, again by an unspecified CVD process (probably by applying dichlorosilane or siloxane followed by pyrolysis). Subsequent CVD application of another tungsten layer apparently consumes the polysilicon layer.

Other than establishing that a tungsten halide will attack silicon, Tsai has little relationship to the process now claimed. Tsai is a CVD process, not an ALD process. Tsai applies thick, rough layers, as is characteristic of a CVD process. Thickness control at the level possible using the claimed process cannot be achieved in Tsai's process. Tsai's process amounts to an attempt to overcome the surface roughness problem of CVD processes by introducing more process steps and complexing to the process. Tsai does not teach or suggest the process the applicants not claim.

Srinivasan describes depositing polysilicon layers, not metal layers. By itself, this reference has little relationship to the process now claimed. The combination of Srinivasan and Tsai does not lead to this invention, either. Srinivasan describes making a polysilicon layer by decomposing silane. If Srinivasan's process was used to make the polysilicon layer in Tsai, the Tsai's process would look like this:

1. First, deposit a silane layer via CVD.
2. Second, thermally decompose the silane layer to form a polysilicon layer.
3. Third, deposit tungsten via CVD, using  $WF_6$  as a reagent, consuming the polysilicon layer in the process.

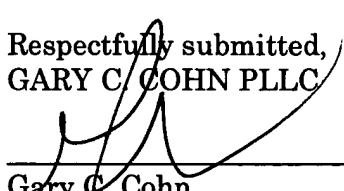
In this process,  $WF_6$  is never reacted with a silylating agent, as required in the applicant's claims. The silane has been converted to polysilicon before the  $WF_6$  is introduced.

Kobayashi describes a CVD process in which  $WF_6$  is reduced to deposit a tungsten film. As discussed above, CVD processes using  $WF_6$  and silanes to produce tungsten films produce poor quality films. No combination of Kobayashi and the other references teaches or suggests the applicant's invention.

Conclusion

Entry of new claims 35 and 36 is requested. All claims now pending in this application have been shown to be novel and unobvious over the cited references. A timely notice of allowance is therefore respectfully requested. The undersigned is available by telephone if a call would advance prosecution.

Respectfully submitted,  
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